Pd/Cu Site Interchange and Non-Fermi-Liquid Behavior in UCu$_4$Pd

C. H. Booth,[1,*] D. E. MacLaughlin,[1,2] R. H. Heffner,[1] R. Chau,[3,†] M. B Maple,[3] and G. H. Kwei,[1]

[1] *Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2] *Department of Physics, University of California, Riverside, California 92521*
[3] *Department of Physics, University of California, San Diego, California 92093*

X-ray-absorption fine-structure measurements of the local structure in UCu$_4$Pd are described which indicate a probable lattice-disorder origin for non-Fermi-liquid behavior in this material. Short Pd-Cu distances are observed, consistent with $24 \pm 3\%$ of the Pd atoms occupying nominally Cu sites. A "Kondo disorder" model, based on the effect on the local Kondo temperature T_K of this interchange and some additional bond-length disorder, agrees quantitatively with previous experimental susceptibility data, and therefore also with specific heat and magnetic resonance experiments.

A number of heavy-fermion f-ion compounds and alloys exhibit low-temperature thermodynamic and transport properties which do not behave as expected from the Landau Fermi-liquid theory thought to be applicable to heavy-fermion systems [1]. Typical non-Fermi liquid (NFL) anomalies at low temperatures include logarithmic or weak power law dependences of the Sommerfeld specific heat coefficient $\gamma(T) = C(T)/T$ and the magnetic susceptibility $\chi(T)$, and a linear temperature dependence of the electrical resistivity $\Delta\rho(T) = \rho(T) - \rho(0)$ rather than the T^2 dependence expected from Fermi-liquid theory. Most but not all NFL materials are disordered alloys, and theoretical treatments of NFL behavior have differed as to whether this disorder is important.

Recent nuclear magnetic resonance (NMR) [2] and muon-spin rotation (μSR) [3] experiments revealed a broad inhomogeneous distribution of the low-temperature local susceptibility in UCu$_{5-x}$Pd$_x$, $x = 1.0$ and 1.5. A phenomenological "Kondo disorder" model can account for the NFL behavior as due to a broad distribution $P(T_K)$ of Kondo temperatures T_K, such that a significant number of f-ion spins with very low T_K remain uncompensated at low temperatures. These uncompensated spins dominate the low-temperature thermodynamic properties and are able to account for the T-linear resistivity [4]. This model also describes the specific heat and susceptibility of the disordered NFL alloy CeRh$_{2-x}$Ru$_x$Si$_2$, $x = 1.0$ [5]. Despite the ability to account for many of the electronic properties of these materials, evidence for the microscopic origin of Kondo disorder is still necessary to confirm that it properly describes the physics of these materials.

The present study aims to determine the extent to which structural disorder may cause Kondo disorder in a nominally ordered NFL system. We chose UCu$_4$Pd for this purpose, since it is well studied [2,3] and has recently been characterized by neutron diffraction [6]. In this diffraction study, Pd is shown to have a strong tendency to occupy the $4c$ site in the cubic $\bar{4}3m$ structure. However, the experiment cannot differentiate between full $4c$ site occupancy by Pd and up to approximately 16% of the $4c$ sites occupied by Cu rather than Pd atoms. Using a simple heuristic model, we estimate below that Pd/Cu site interchange of this magnitude may be enough to cause sufficient Kondo disorder to explain the NFL behavior. A better measurement of the amount of site interchange is difficult for neutron measurements, since the contrast between the coherent scattering lengths for U (8.4 fm), Pd (5.9 fm), and Cu (7.7 fm) is not large.

A better way to determine the extent of any Cu/Pd site interchange in UCu$_4$Pd is to use a local probe to look at the near-neighbor bond-length distributions. If Pd atoms sit on some Cu sites, for instance, there will be Pd-Cu distances at ~ 2.50 Å overlapping Cu-Cu pairs at the same distance. It is therefore vitally important to use a probe that is atomic-species specific. For this reason we have performed x-ray-absorption fine-structure (XAFS) experiments on the same sample of UCu$_4$Pd used in Ref. [6], using the U L_{III} edge and the Pd and Cu K edges.

Details of the sample-growth procedure are given in Ref. [6]. After the μSR experiments [3], approximately 200 mg of a pellet was soaked in methanol to remove a binding varnish, and reground by hand in acetone. The average particle size was estimated from microscopy to be $\sim 20\mu$m. In addition, the sample was passed through a 20 μm sieve for the Cu-edge experiment. The sample was then brushed onto scotch tape, and layers of the tape were stacked to produce a change in the absorption coefficient of approximately unity.

X-ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory from the U L_{III} and Pd K edges at BL 10-2 using Si(220) detuned double monochromator crystals. The Cu K-edge data were collected at BL 2-3 with Si(111) crystals, similarly detuned. The vertical slit height was set at 0.7 mm. Data were collected at $T=3.3$ K for the U and Pd edges, and at $T=$ 20 K for the Cu edge, with the temperature controlled within 0.1 K. Two scans each were taken for the U and Pd edges, while three scans were collected for the Cu edge data. More scans were collected at temperatures ranging

up to 320 K; these will be discussed in a future article. The absorption data were reduced using standard procedures [7], which include fitting an embedded-atom absorption $\mu_0(E)$ with a 5 knot spline function. The XAFS function $\chi(k)$ is defined as $\mu(k)/\mu_0(k)-1$, where μ is the absorption coefficient, $k = \sqrt{2m_e/\hbar^2}(E-E_0)$ is the photoelectron wave vector, m_e is the electron rest mass, and the ionization threshold energy E_0 is chosen arbitrarily as the energy at the half-height of the absorbing edge, and is allowed to vary in subsequent fits.
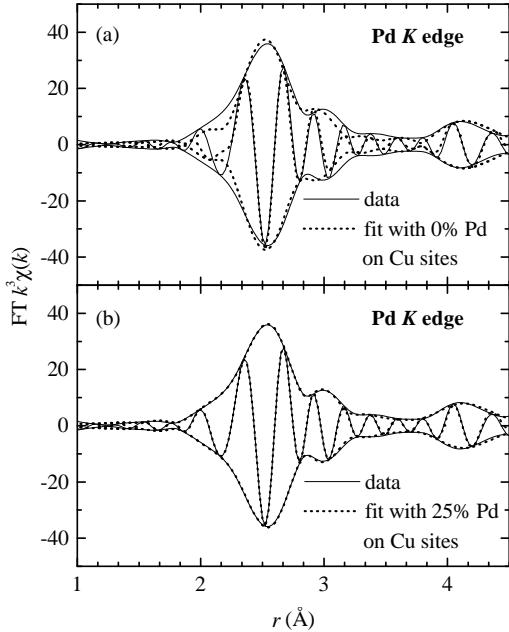

FIG. 1. Fourier transform (FT) of $k^3\chi(k)$ from the Pd K edge. The outer envelope is the amplitude and the oscillating inner line is the real part of the complex transform. Solid lines are data taken at $T=3.3$ K, and the dotted lines are fits assuming (a) only bonds found in the nominally ordered structure, and (b) also bonds consistent with Pd on Cu sites. Transforms are from 3.0-14.5 Å^{-1}, and Gaussian broadened by 0.3 Å^{-1}. Fits are from 2.0 to 4.5 Å.

XAFS provides information about the atomic arrangement of near neighbor atoms to an absorbing atom. The XAFS function $\chi(k)$ has oscillations due to the interference of the outgoing photoelectron and the component back scattered to the absorbing atom. By fitting with theoretical calculations of the back-scattering amplitude and phase for each shell [8] we can determine the parameters S_0^2, N_i, R_i, and σ, defined as follows. S_0^2 is an amplitude reduction factor, which is poorly determined by theory and is therefore fit somewhat arbitrarily. It is correlated in the fits with the number of neighbors in the ith shell N_i, so we hold N_i fixed whenever possible. The bond length to the ith shell R_i and the distribution width σ_i of this shell are better determined. More details of fitting procedures are found in Ref. [7].

Before describing the data, we first recall that the crystal structure of UCu$_4$Pd can be described as interlocking U and Pd fcc lattices, with an interstitial vertex-sharing network of Cu tetrahedra. From a local perspective, the U and Pd sites are very similar. Each site has twelve Cu neighbors at 2.93 Å made up from the faces of four Cu tetrahedra, and four Pd (for U sites) or U (for Pd sites) neighbors at 3.06 Å. The local Cu environment is made up of four Cu-Cu pairs at $\sim$ 2.50 Å and four each Cu-U and Cu-Pd pairs at $\sim$ 2.93 Å.

Since the Pd K-edge data determine the model we will use for the distortion, we start with a discussion of these data and then present the U and Cu edge results. First consider a fit to the data that does not include any site interchange. We assume that the N_i are given by the ordered structure, so that the overall amplitude is given only by S_0^2 and the widths σ_i for the individual shells. Such a fit is displayed in Fig. 1(a). The main peak in this transform at $\sim$ 2.6 Å is primarily due to the Pd-Cu pairs, which are separated by 2.93 Å. (Peaks in XAFS transforms are shifted from the atom-pair distances by a phase shift of the photoelectron at both the absorbing and the back-scattering atoms). The shoulder on the right side is from the Pd-U path at 3.06 Å. This fit is of very poor quality, particularly on the low side of the main Pd-Cu peak. If we then allow for a model with some Pd on the Cu sites (the main effect arises from adding a Pd-Cu bond at $\sim$ 2.50 Å), we are much better able to fit the low side of the main peak. In fact, the fit [Fig. 1(b)] converges with bond lengths for the extra added peaks which are very close to the bond lengths from the copper site. Using this fit as a reference, the undistorted fit has a worse statistical-χ^2 by over 3000%! Moreover, since each back-scattering atomic species has a distinctive phase and back-scattering amplitude, we know that the extra peaks indeed involve the species consistent with Pd/Cu site interchange. We estimate the fraction of Pd atoms that reside on Cu sites to be $24 \pm 3\%$.

Fits to the U and Cu edge data are more ambiguous about the Pd/Cu site interchange observed from the Pd edge. The signal from the more abundant Cu atoms and overlapping shells make fits that include Pd/Cu site interchange only slightly better than those that do not. U/Cu site interchange, on the other hand, should be detectable from the U edge data by observing a short U-Cu peak. We measure no such peak, and place a limit of $\leq 10\%$ of the U atoms on Cu sites. All these fits are consistent with the average structure determined by diffraction, and are the same quality as the fit in Fig. 1(b).

Based on the measurements presented above, we now know that a significant fraction of the Pd atoms ($\sim$ 1/4) sit on the nominally Cu 16e sites, indicating that this system is not intrinsically homogeneous. This result therefore strongly suggests the applicability of Kondo disorder models for UCu$_4$Pd, and that the microscopic origin of this disorder is structural. With this knowledge, we are

compelled to ask, is the measured amount of disorder consistent with the observed NFL behavior?
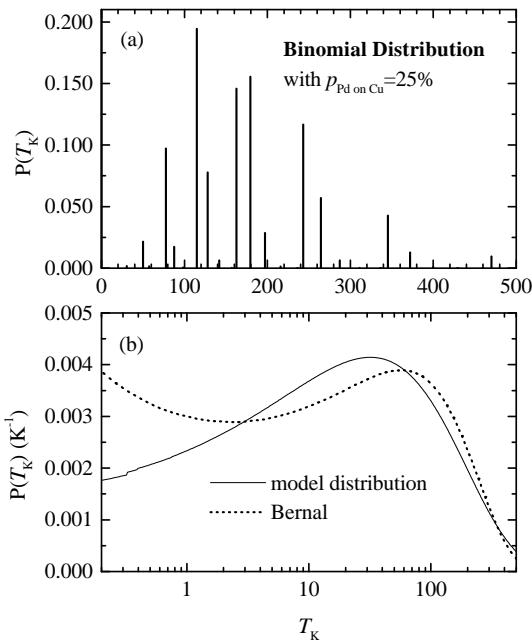

FIG. 2. (a) Distribution of T_K's based on 25% probability of a given Pd on a Cu site, as described in the text. (b) Distribution for (a) with 0.047 Å additional bond length disorder. The distribution from Ref. [2] is shown for comparison.

To answer this question, we calculate a distribution of Kondo temperatures $P(T_K)$, and from this distribution and a Bethe-ansatz calculation of the susceptibility of single Kondo impurity, we calculate the susceptibility $\chi(T, P(T_K))$. We apply disorder in a local fashion to the Kondo temperature:

$$T_K = E_F e^{-1/(\rho \mathcal{J})}, \qquad (1)$$

where E_F is the Fermi energy, ρ is the density of states at the Fermi level and $\mathcal{J}$ is the conduction-electron/local-moment exchange energy. We hypothesize that ρ is primarily a long-range quantity, and consider only disorder in $\mathcal{J}$. To this end, we employ a tight-binding formula [9] for the coupling energy between the electronic shells of neighboring atoms. The dominant contribution is from $f-d$ hybridization, given by:

$$V_{fd} = \frac{\eta_{fd} \hbar^2}{m_e} \frac{(r_{Uf}^5 r_{Xd}^3)^{1/2}}{R_{U-X}^6}, \qquad (2)$$

where $r_{X\ell}$ is the radius of the electronic shell with angular momentum ℓ for atom X (tabulated in Ref. [10]), and R is the bond length between the atoms with $\ell = f$ and d. The coefficient η_{fd} depends only on the ℓ's and the bond symmetry (see Appendix B in Ref. [9]). We will assume all bonds are σ-bonds. This coupling energy is related to the exchange energy in Kondo theory simply by $\mathcal{J} = V_{fd}^2/\epsilon_f$, where ϵ_f is the f-level energy. Within this tight-binding approach, calculated energies are often too high compared to experiment by a factor of two [9].

As our basic model of the lattice, we sum Eq. (2) over U-X pairs that have a significant hybridization V_{fd}. These include the twelve nearest neighbor U-Cu pairs at 2.93 Å, and the four U-Pd pairs at 3.06 Å. In fact, the hybridization per bond is higher for the U-Pd pairs because the radius of the d shell of Pd is nearly 50% larger than that of Cu. To this base structure, we then allow each Pd site to have a 25% chance of having a Cu atom on it, and each Cu site to have a 6.25% (25/4) chance of having a Pd on it. The effect of Pd on Cu sites is to raise the local hybridization, and thus the local T_K. Replacing Pd with Cu on Pd sites has the opposite effect. All the different possible configurations and their probabilities (as given by a binomial distribution) were calculated. The resulting discrete distribution of T_K's is shown in Fig. 2(a). We use E_F from Ref. [2] and ρ/ϵ_f =7.27 eV^{-2}, as described below. Notice that there is no mechanism within this model to provide any weight within the binomial model at T_K near 0 K; Fig. 2(a) reflects this inadequacy.

In order for this model to be complete, however, we must also consider the effect of bond length disorder on the hybridization, as occurs from normal (Debye) vibrations and possibly other static or dynamic origins. We estimate this disorder for an arbitrary distribution of V_{fd} by calculating an average bond length R' (assuming r_d for Cu) and convolving Eq. (2) with a distribution of bond lengths with half-width σ. We write the pair-distribution function as $N_\phi e^{-\phi(r)/(k_B T)}$, where N_ϕ is a normalization factor and $\phi(r)$ is a suitable interatomic potential. We choose a Lennard-Jones potential rather than a harmonic or a Morse potential because it models the hard-core repulsion and still only has two input parameters. We define the position of the peak in the distribution as R' and the inverse of the coefficient of the second-order term as σ^2. Convolving this distribution with any V_{fd}, one finds the spread in T_K's to be surprisingly large. To illustrate the magnitude of this effect, consider the case of UCu$_4$Pd without site interchange (contrary to our measurement), but with a modest amount of static disorder. We estimate as little as $\sigma = 0.01$ Å of static disorder generates a spread of Kondo temperatures $\sigma_{T_K}/\langle T_K \rangle \sim 40\%$.

We calculate $\chi(T, P(T_K))$ by convolving the present $P(T_K)$ using 25% site interchange and bond length disorder σ with a theoretical $\chi(T, T_K)$ using the Bethe ansatz [11]. This curve is for a J=3/2 state with a Landé g-factor of 1.8745, and we hold $E_F = 1.41$ eV, as used in Ref. [2]. This procedure requires ρ/ϵ_f and σ as fitting parameters. We fit this distribution to the susceptibility derived from the $P(T_K)$ in Ref. [2], since it is continuous and essentially fits the data exactly down to ~ 2 K. The results for the final fit parameters are $\rho/\epsilon_f = 7.27 \pm 0.07$ eV^{-2} and $\sigma = 0.047 \pm 0.002$ Å. The

3

latter parameter is within the range of the static distortion estimated from the U L_{III}-edge data. Indeed, some level of static disorder is expected for a system with such a high degree of site interchange. However, the amount of Pd/Cu site interchange and σ are very strongly correlated such that good fits are obtainable even with no site interchange and a slightly larger (~ 0.002 Å) value of σ. Therefore, we cannot use the susceptibility data alone to determine the amount of site interchange.
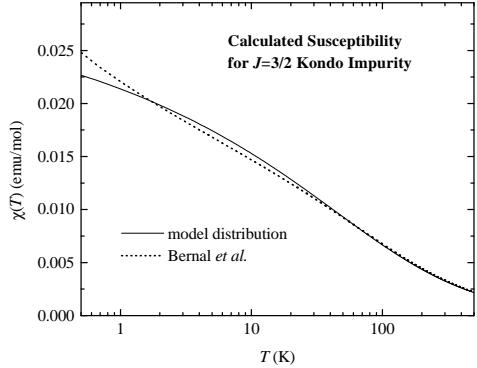
FIG. 3. Magnetic susceptibility $\chi(T)$ calculated by convolving $P(T_K)$ from Fig. 2(b) with a $J=3/2$ impurity from Ref. [11].

The final $P(T_K)$ distribution is shown in Fig. 2(b) and the susceptibility fits are shown in Fig. 3. The agreement between the susceptibility curves is very good for T_K larger than ~ 1 K. Since the actual data only go down to ~ 2 K, the distribution we are testing is consistent with these data. In any case, the discrepancy between the models may be difficult to interpret since it depends on the theoretical calculations for both the susceptibility of a Kondo impurity and the $f-d$ hybridization.

Despite these shortcomings, the present model has some good fundamental features that differ from the previous model used in Ref. [2]. One difference is that the present distribution of $\rho\mathcal{J}$ is chosen from a microscopic model based on experiment, rather than arbitrarily chosen to be Gaussian. The choice of a Gaussian causes $P(T_K)$ in Ref. [2] to diverge as $T_K \to 0$ K. The distribution used in the present work cannot diverge as $T_K \to 0$ K because $V_{fd} \to 0$ only for $R \to \infty$. This lack of divergence should cause $\chi(T)$ as $T \to 0$ K to reach a limiting value. Such behavior has in fact been observed at temperatures below ~ 0.2 K [12], although we do not consider the alleged spin-glass behavior. Finally, we must point out that more sophisticated models of Kondo disorder, such as the recently proposed Griffiths phase [13] are possibly consistent with the work presented here.

In summary, we have measured the local structure around U, Cu, and Pd atoms using XAFS in UCu$_4$Pd. The Pd data show a significant number of Cu bonds at a distance consistent with 25% of the Pd atoms on Cu (16e) sites. This level of lattice disorder strongly suggests the Kondo disorder model as a starting place for understanding NFL behavior in this compound. To test this assertion, we present a model of the distribution of Kondo temperatures assuming a binomial distribution of Pd on Cu sites (and vice versa), together with some disorder in the mean bond length around each U atom. Hybridization strengths are calculated assuming a tight-binding model. The model is shown to yield a susceptibility quantitatively similar to the measured $\chi(T)$ of Ref. [2]. Since the specific heat, NMR and μSR results can also be described in terms of $P(T_K)$ [2,3], this model can describe many of the electronic properties. This ability combined with the Cu/Pd site interchange measurements is very strong evidence in favor of lattice disorder as the microscopic mechanism of NFL behavior in UCu$_4$Pd.

* email: cbooth@lanl.gov.

† Present address: Lawrence Livermore National Laboratory, Livermore, California 94550.

[1] See, for example, articles in *Proceedings of the Conference on Non-Fermi Liquid Behavior in Metals*, Santa Barbara, California, 1996, edited by P. Coleman, M. B. Maple, and A. J. Millis, J. Phys.: Condens. Matter **8** (1996).

[2] O. O. Bernal *et al.*, Phys. Rev. Lett. **75**, 2023 (1995).

[3] D. E. MacLaughlin, O. O. Bernal, and H. G. Lukefahr, J. Phys. Condens. Matter **8**, 9855 (1996).

[4] E. Miranda, V. Dobrosavlijević, and G. Kotliar, J. Phys. Condens. Matter **8**, 9871 (1996); E. Miranda, V. Dobrosavlijević, and G. Kotliar, Phys. Rev. Lett. **78**, 290 (1997);

[5] T. Graf *et al.*, Phys. Rev. Lett. **78**, 3769 (1997).

[6] R. Chau, M. B. Maple, and R. A. Robinson, Phys. Rev. B **58**, 139 (1998).

[7] G. G. Li, F. Bridges, and C. H. Booth, Phys. Rev. B **52**, 6332 (1995).

[8] S. I. Zabinsky *et al.*, Phys. Rev. B **52**, 2995 (1995).

[9] W. A. Harrison and G. K. Straub, Phys. Rev. B **36**, 2695 (1987).

[10] G. K. Straub and W. A. Harrison, Phys. Rev. B **31**, 7668 (1985).

[11] V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[12] R. Vollmer *et al.*, Physica B **230-232**, 603 (1997).

[13] A. H. Castro Neto, G. Castilla, and B. A. Jones, cond-mat/971023.